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THE TWO COMMON FAILURES OF THE CLARK STANDARD CELL

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By E. C. McKelvy and M. P. Shoemaker

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I. INTRODUCTION

The International Electrical Congress, which met in Chicago in 1893, fixed the numerical magnitudes of the three fundamental units which enter into Ohm's law. These were designated as the *international ohm*, the *international ampere*, and the *international volt*. The *international volt* was defined as "the electromotive force that, steadily applied to a conductor whose resistance is one international ohm, will produce a current of one international ampere, and which is represented sufficiently well for practical use by $\frac{1000}{1434}$ of the electromotive force between the poles * * * of the voltaic cell, known as Clark's cell, at a temperature of 15° C * * *."

The United States, Canada, Great Britain, and France, in the order named, legally adopted the definition of the international volt substantially as above defined. Germany defined the international volt in terms of the ohm and ampere only and did not include in its law a value for the Clark cell. Because of greater ease and practicability, the practice in all countries, including Germany, has been to fix the volt by reference to standard cells, and up to 1908 the Clark standard cell was in effect the international working standard of electromotive force in all the above-mentioned countries.

During the 15 years that intervened between the Chicago Congress and the International Conference on Electrical Units and Standards, London, 1908, an enormous amount of research work on both Clark and Weston standard cells was done by the national standardizing laboratories of England, Germany, France, and the United States, and by individuals, particularly during the latter half of this period. This work showed the cadmium (Western) cell to possess certain advantages over the zinc (Clark) cell, and for this reason the saturated Weston cell or Weston normal cell was officially adopted by the London Conference as the Standard of electromotive force, superseding the Clark cell.

It has been observed at the Bureau of Standards [1] and elsewhere [2] that Clark standard cells in general exhibit less change in value with time than do Weston cells. Aside from the larger temperature coefficient, an admitted disadvantage which, however, assumes less importance with the modern developments in accurate temperature control, two serious defects develop in Clark cells which render them less desirable as reference standards of electromotive force than Weston cells. These two defects make the average life of Clark cells much shorter than that of Weston cells, when both types are set up using similar precautions and maintained under the same conditions.

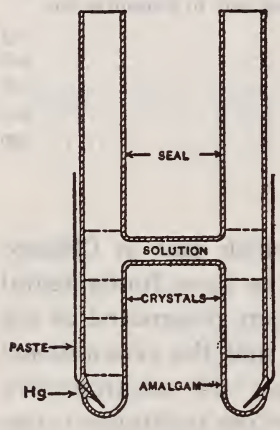


FIG. 1.—*Ordinary H-form cell blank*

It is generally recognized that the glass H-type of cell blank, shown in Fig. 1, with sealed-in terminals, gives, when hermetically sealed, results that are entirely satisfactory from the standpoint of mechanical permanence when used for cadmium cells. When used for zinc cells, however, it is prone to failure through cracking of the wall at the amalgam terminal. If the cell be hermetically sealed, in which case the interior of the cell may be under some-what reduced pressure, the effect of the cracking is to admit oil or air, depending on whether the cell is in or out of a constant-temperature bath. In either case the crystals are lifted from the surface of the amalgam, and the internal resistance of the cell becomes practically infinite.

[1] Wolff and Waters, B. S. Bulletin, 4, p. 71; 1907–8. [2] Hulett, Phys. Rev., 32, p. 275; 1911.

Another defect, inherent in the zinc cell and rarely observed in the cadmium cell, is the gradual accumulation of gas above the amalgam, resulting in increasing internal resistance and often eventually in interruption of the electrical continuity of the cell.

The purpose of the present work is the study of the causes of the above two types of failure and the determination of methods of eliminating them, thus placing Clark cells on the same basis as Weston cells from the standpoint of length of life, a very important factor to be considered in the maintenance of a permanent standard of electromotive force. An auxiliary reference set of zinc cells, if kept intact, would certainly prove of value in the maintenance of such a standard.

II. GENERAL DISCUSSION

1. THE EXTENT OF FAILURES

The seriousness of the failures in zinc cells with relation to their value as permanent standards is shown by the fact that 120 out of 128, or approximately 94 per cent, of such cells set up in 1906 in ordinary H blanks and kept at this bureau, are to-day useless because of one or both of the above-mentioned defects.

The literature on this subject also shows the gradual dropping out of zinc cells in long-period observations of a group, presumably because of the development of the same defects. Jaeger and Kahle,[3] for example, in November, 1897, were able to obtain measurements on but 9 of a group of 20 zinc cells set up between November, 1891, and February, 1893. At the same time, November, 1897, they were able to obtain measurements on 31 of a group of 34 cadmium cells set up between April and December, 1894, thus showing the striking difference in the permanence of the two types of cells.

Seven out of 13 zinc cells set up by Rayleigh and Sidgwick[4] between February and July, 1884, had failed before December of the same year. Rayleigh[5] later reported that but 3 of these cells could be measured two years after setting up.

Standard zinc cells were first hermetically sealed in glass by Wright and Thompson[6] in a study of the effect of dissolved air on the electromotive force. These were of the inverted-Y type. Such cells were kept intact for two years. Cells completely embedded in paraffin also kept intact for two years. When cells

[3] Zs. f. Instrk., **18**, p. 161; 1898. Wied. Ann., **65**, p. 928; 1898.
[4] Phil. Trans., **175**, pp. 411–460; 1884.
[5] Phil. Trans., **176**, pp. 781–800; 1885.
[6] Phil. Mag., **16** (5), pp. 25–48; 1883.

were merely sealed with a plug of paraffin, cracks soon developed, either in the paraffin or between the paraffin and glass. The negative limb in these cells consisted of a zinc rod partly embedded in paraffin, the attached platinum wire also embedded, being sealed through the glass.

2. CRACKING

Rayleigh and Sidgwick[7] in 1884, using zinc amalgam in the H-form of cell, were probably the first to observe the cracking of the amalgam limb of the cell and erroneously ascribed it to the expansion of the amalgam through the formation of hard, compact lumps. They concluded that the addition of zinc to the fluid amalgam had better be omitted. This view was corrected the next year by Rayleigh,[8] who found that the glass cracked even when using amalgams containing very little solid phase. The cracking is ascribed to the alloying of the zinc amalgam with the platinum wire and its resultant increase in diameter. As a remedy, Rayleigh proposed that a little cement be applied as a protective coating to that portion of the terminal wire lying nearest the glass. No report was made as to the adequacy of this remedy, but our own results indicate that a slight retardation of the alloying action is the most that could be hoped for, and this only at the expense of probable contamination of the cell by the cement.

The general practice at this Bureau and elsewhere has been to seal the terminal wire through the cell wall in such a way as to leave all but the end of the wire within the cell covered by a thin sheath of glass. This method of sealing in, already described by Hulett,[9] was thought to render the cell less liable to crack, particularly if fine wire was used. However, with the smallest size platinum wire practicable for use as terminals, the sheath of glass has afforded little or no protection against cracking of the amalgam limb of zinc cells.

3. GAS FORMATION

The formation of gas in the amalgam limb of the zinc cell seems to have been observed first by Schuster,[10] since in constructing a large cell at Manchester in July, 1891, a mercury valve was provided to permit the escape of gas if evolved. Its causes were

[7] Phil. Trans., **175**, p. 443; 1884.
[8] Phil. Trans., **176**, p. 784; 1885.
[9] Phys. Rev., **32**, pp. 271–272; 1911.
[10] Glazebrook and Skinner, Phil. Trans., **183**, p. 588; 1892.

considered first by Kahle,[11] who observed that increased evolution of gas occurs with free acid in the zinc sulphate solution; also with impure zinc, particularly if it contains arsenic. In the latter case the formation of gas is ascribed to local currents within the amalgam and is said to have occurred when the purest of zinc salt was employed. Where the pure zinc and pure neutral salt were used, no evolution of gas had been observed by Kahle at the time of writing. Inasmuch as this investigator[12] and other investigators at the Physikalisch-Technische Reichsanstalt later mention trouble resulting from this type of failure, it is safe to conclude that, with the purest materials they were able to obtain, the difficulty was not entirely obviated.

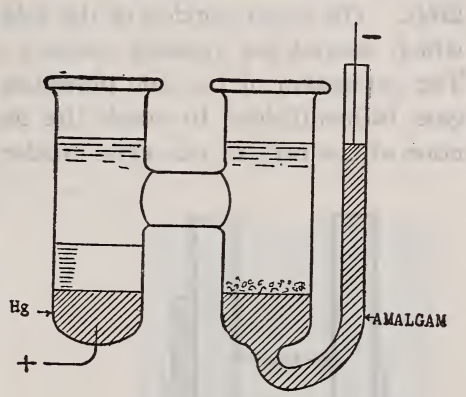


FIG. 2.—*Form of Clark cell proposed by Jaeger*

Our experience shows that even with materials of unquestionable purity the evolution of gas is often sufficient to cause lifting of the crystals and interruption of the electrical continuity of the cell.

4. FORMS OF CELLS DESIGNED TO ELIMINATE CRACKING AND TO MINIMIZE THE EFFECTS OF GAS FORMATION

Practically all workers on the zinc cell have been troubled by the two types of failure considered. A discussion of these is given by Jaeger,[13] who used the form of cell shown in Fig. 2 to obviate cracking. In this the hot zinc amalgam is drawn up into the side tube and the platinum terminal is inserted while the amalgam is still in the molten condition. Such cells were evidently not hermetically sealed. A form of cell (Fig. 3) very similar to that above, but one which was intended to be sealed hermetically, was employed by Wolff and Waters.[14] It was thought that, by having only the lower half of the platinum wire covered by the amalgam, the cracking of the glass at the sealing-in point would be prevented. This did not prove to be the case, however. It was subsequently observed that amalgam would

[11] Zs. f. Instrk., **13**, pp. 293–314; 1893.
[12] Jaeger and Kahle, Zs. f. Instrk., **18**, p. 161; 1898. Wied. Ann. **65**, p. 926; 1898.
[13] Die Normalelemente, p. 56; 1902.

creep along platinum wire a distance of more than 5 cm., breaking the glass rod into which it has been sealed along the entire length, as clearly shown in *A*, Fig. 5.

Another form of cell employed by F. A. Wolff at this Bureau is shown in Fig. 4. In this a very fine platinum wire is sealed into a glass partition separating the side tube and the amalgam limb. The lower portion of the side tube was filled with mercury, which served for making contact with the fine sealed-in wire. The expansion of the fine platinum wire on absorbing the amalgam is insufficient to crack the mass of glass about it. While none of the cells of this type cracked, they did not prove entirely

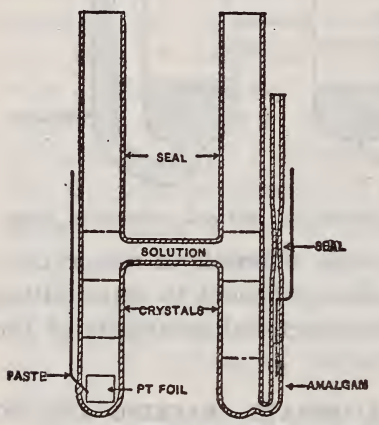


FIG. 3.—*Form of Clark cell devised by Wolff and Waters. Scales of Figs. 3 and 4 differ.*

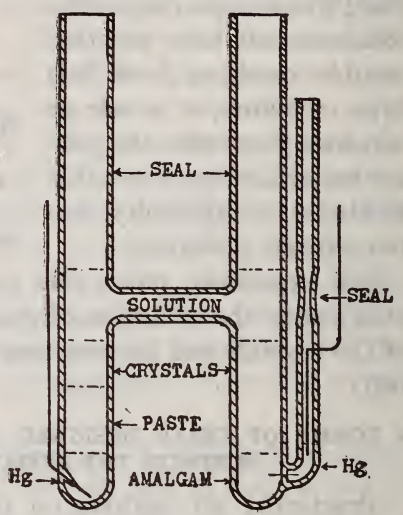
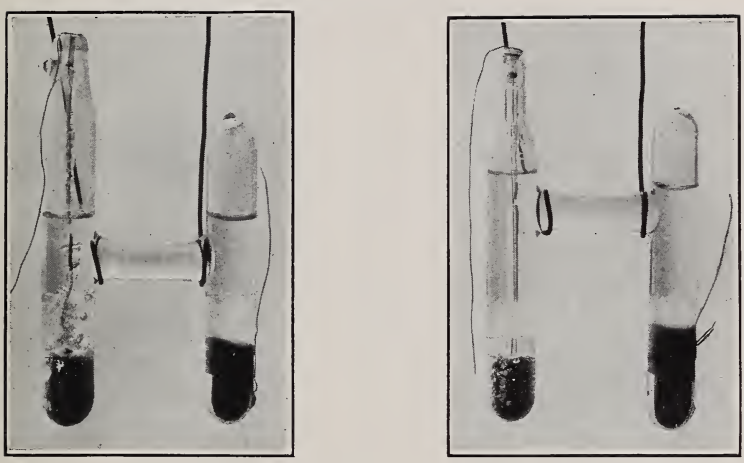


FIG. 4.—*Form of Clark cell devised by Wolff*

satisfactory, principally because of the difficulty experienced in getting a reliable contact between the side limb and the cell proper. The resistance of these cells, high to start with, was found to increase greatly, probably because of the formation of a slight amount of gas about the fine sealing-in wire.

In December, 1910, a number of cells of the type shown in Fig. 5 were set up in an attempt to obtain hermetically sealed cells with removable amalgam terminal wires. All that was necessary was to crack the top of the cell limb about the amalgam terminal, withdraw the cracked electrode, replace it with a new one, and reseal. This would at the same time permit the escape of any gas that might have formed in the cell. Two types of amalgam electrodes are shown in Fig. 5. In *A* the wire is sealed

[14] B. S. Bulletin, 3, p. 636; 1907.



A *B*

FIG. 5.—*Hermetically sealed cells with removable amalgam terminals*

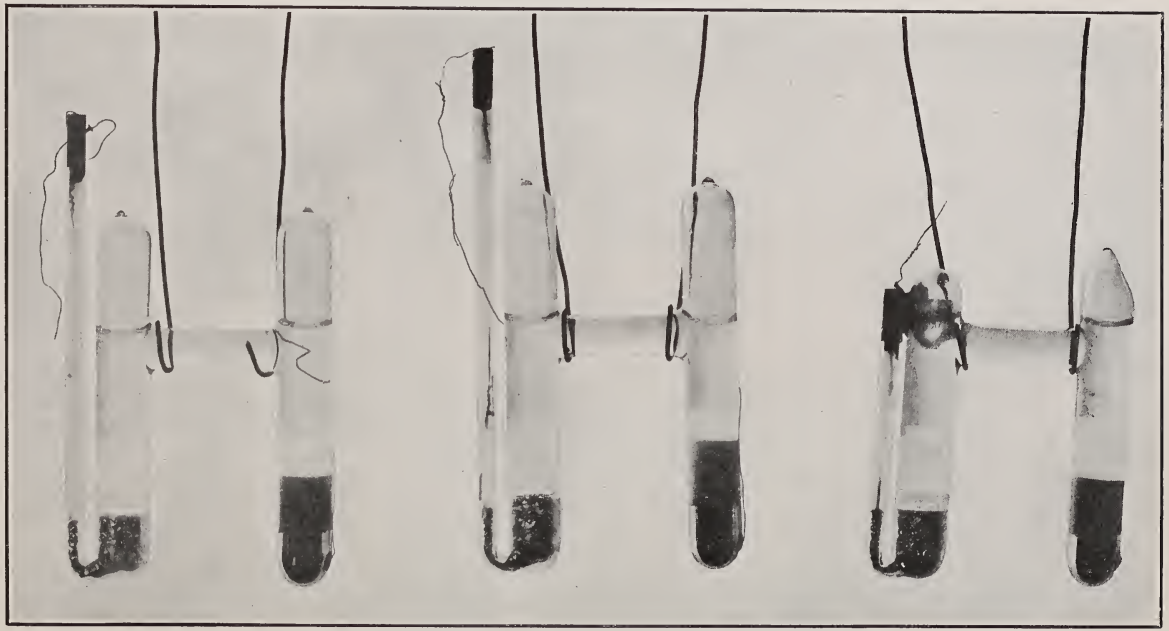


FIG. 6.—*Clark cells, illustrating the effect of gas formation*

through a solid rod of glass, and in *B* it is sealed through a glass tube and is free of the tube walls except at the ends and in the middle. However, the life of the terminals was so short and the extent of the cracking so severe (*A* in Fig. 5) that this method of construction was not considered a practical or satisfactory means of securing minimum disturbance within the cell.

In July, 1912, a number of cells of the type shown in Fig. 6 were set up. In these the amalgam in the side tube did not extend beyond the level of the amalgam within the cell proper. Molten paraffin was poured about the terminal wire to within a centimeter of the top of the side tube and the tube then sealed with Khotinski cement, which is similar to marine glue. These cells are still in good condition as far as cracking or leakage is concerned; but there is always more or less danger of oil seeping in, since it is difficult to make a perfect and lasting seal of the character described. The cells in the figure are shown here primarily to illustrate the effect of gas formation.

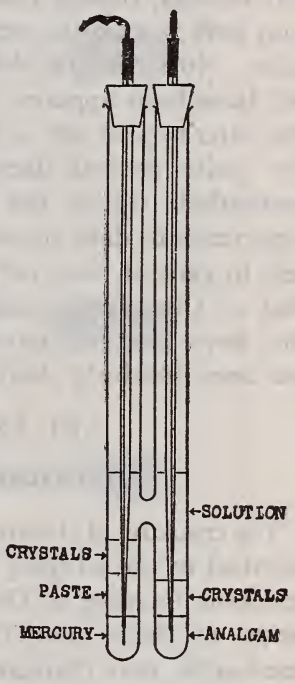


FIG. 7.—*Hulett form of cell with cork seals and removable electrodes*

A partially successful attempt to obviate the effects of cracking and gas formation was made by Hulett.[15] Recognizing the desirability of making the cell contents readily accessible, owing both to the formation of gas and the caking of the zinc-sulphate crystals, the platinum wire electrodes are introduced through corks, as shown in Fig. 7. This construction permits of ready withdrawal and renewal of the electrodes when cracked, the breaking up of any cake of crystals formed, and the consequent liberation of gas, with a minimum disturbance of the cell. All these advantages and conveniences and certain additional ones are obtained, however, at an unquestionable sacrifice of permanency and freedom from outside disturbing influences, advantages that are inherent in the hermetically sealed cell.

Hulett[16] has observed the cracking of the glass about the platinum wire in both limbs of both zinc and cadmium cells of the

[15] Phys. Rev., 32, pp. 272–275; 1911.

[16] Phys. Rev., 32, p. 274; 1911.

usual H-form, most frequently, however, in the amalgam limb of the zinc cell. Since this phenomenon has not been generally observed by workers in this field except for the zinc-amalgam limb and has not occurred at all in the cathode limb of zinc cells set up at this Bureau, it seems possible that the cracking observed by Hulett was due to faulty construction of the cell blanks, possibly through insufficient annealing. No appreciable amount of gas has been observed in either limb of the cadmium cells at this Bureau, though this would seem likely to occur in the amalgam limb in case the acidity of the cadmium sulfate solution was high. No structural defects comparable with those of the zinc cell have been apparent in cadmium cells. The sole objection to the latter type of cell, so far as permanency is concerned, is its slow but quite general decrease in electromotive force with time, particularly during the first few months after setting up. Our experience to date shows that the electromotive force of the zinc cell, in general, does not decrease as rapidly nor as much as does that of the average cadmium cell, though it must be admitted that fewer zinc cells have been set up and the average life of these has been relatively short.

III. EXPERIMENTAL WORK

1. CRACKING OF THE AMALGAM LIMB

The cracking of the amalgam limb of zinc cells has been correctly ascribed to the alloying of the amalgam with the platinum and a resultant increase in the diameter of the wire. A quarter of a meter of clean, new Heræus platinum wire of approximately one-fourth mm diameter was carefully calipered, subjected to the action of warm 10 per cent zinc amalgam for a few days, and again carefully calipered. The mean diameter of the wire was found to have increased by 0.043 mm, more than 17 per cent. Experiments showed that the expanded wire could be heated in a bunsen flame to red heat for an appreciable time without materially decreasing its diameter, but prolonged heating or heating to a higher temperature resulted in reducing the size of the wire. It was evident that the alloyed and expanded wire could be sealed into glass in the usual way.

In order to test the relative suitability of various available sealing-in glasses, and to test the use of the alloyed and expanded wire sealed in these glasses and in contact with zinc amalgam, small test specimens were set up in March, 1913, as shown in

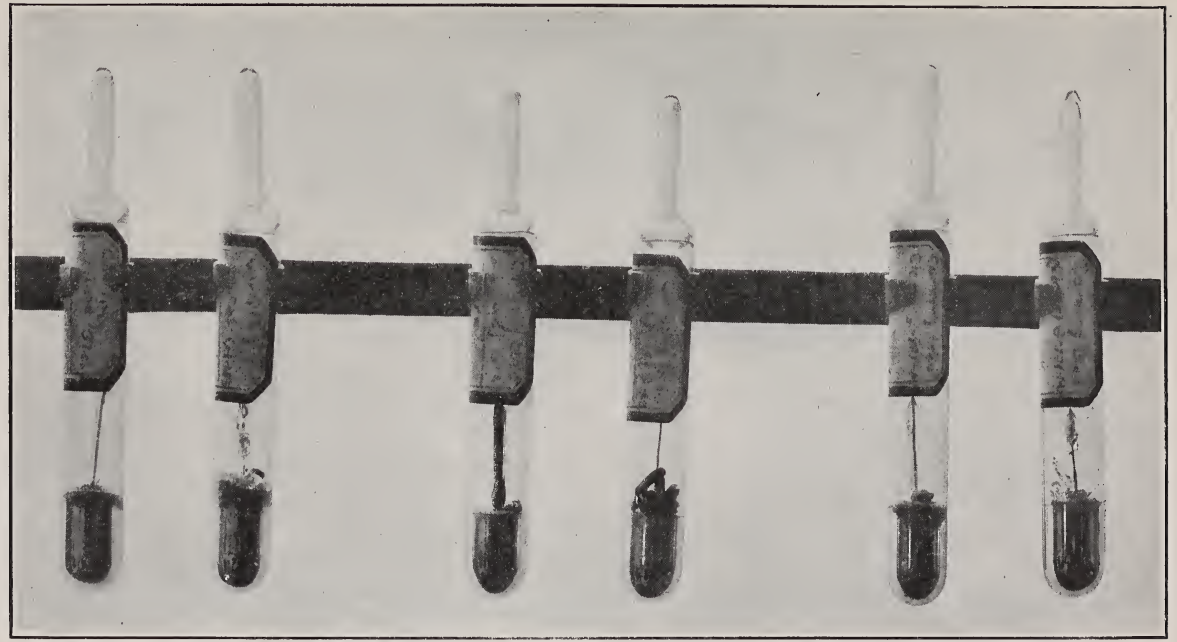
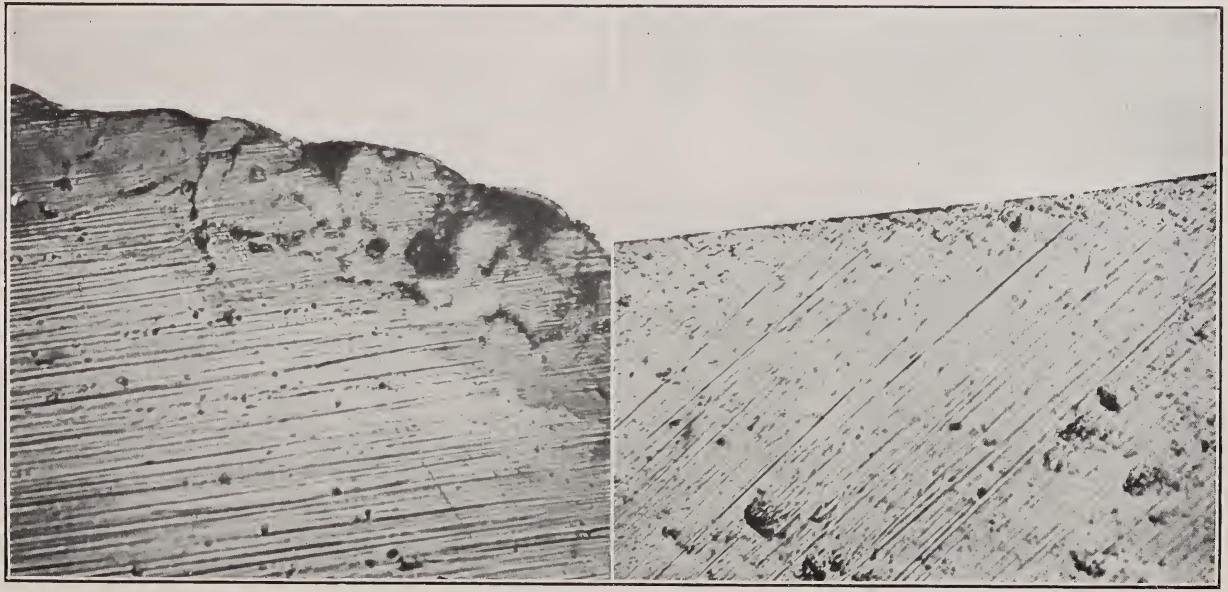


FIG. 9.—*The effects of the action of zinc amalgam on platinum-in-glass seals*



A *B*

FIG. 10.—*Photomicrographs of alloyed* (*A*) *and unalloyed* (*B*) *platinum wire.* × 500

Fig. 8. Alloyed and unalloyed wires were sealed into seven different glasses, as follows: Jena 16^{III}, Jena 397^{III}, Corning G–70, Corning lead, Corning lead (clear) G–901–m_2, Corning lead (red) G–25, and a German sealing-in glass. The last four of these glasses sealed about the untreated wire shattered within a few weeks, and two others, Corning G–70 and Jena 16^{III} were found cracked at the end of six months. The seal made with Jena 397^{III} glass is still in good condition. None of the seven glasses sealed about the *prealloyed* wire have cracked. Fig 9 clearly illustrates the results obtained with three of the Corning glasses. In the left one of each pair of test samples prealloyed wire was used, while in the corresponding one to its right the wire was untreated.

The tendency of platinum to alloy with zinc and the tenacity with which the latter is held is well known.[17] Experiments made at this Bureau show that at room temperature zinc will creep along a platinum wire that has had one end immersed in the molten metal. This creeping is very slow and has not resulted in the shattering of the glass into which the wire was sealed. The penetration of the zinc is much more rapid at higher temperatures and in the presence of mercury.

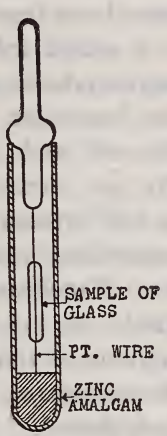


Fig. 8.—*Method of testing platinum-in-glass seals*

In Fig. 10 are photomicrographs of alloyed and unalloyed platinum wire, magnification 500 diameters. *A* shows the alteration of the structure of platinum by the action of the zinc amalgam. As shown, the alteration is confined to the surface because of the fact that the sample of wire used was large in diameter and had been subjected to the action of the amalgam, but a relatively short time. The alloy layer in many places is full of fissures and quite porous.

Two groups of zinc (Clark) cells were set up by the authors with the particular object of avoiding cracking of the amalgam limb. The first group, set up in 1912, consisted of 20 cells of the type already described, and shown in Fig. 6. While all of these cells are still free from mechanical defects, most of them have long been practically useless because of excessive gas formation. In the second group are 18 cells of the usual H-form, but

[17] Deville and Debray, Ann. Chem. Phys., **56** (3), p. 385; 1859. C. R. Acad. Sci., Paris, **94**, p. 1557; 1882. Heycock and Neville, Jr. Chem. Soc., London, **71**, p. 383; 1897. Villiers and Borg, C. R. Acad. Sci., Paris, **116**, p. 1524; 1893. Mylius and Fromm, Ber. Chem. Ges., **27**, p. 630; 1894.

with negative terminals of platinum wire which had been subjected to the action of zinc amalgam before sealing into the cell wall. These cells were set up in 1916, and at the present writing none of them have cracked at the amalgam seal.

2. GAS FORMATION

The formation of hydrogen gas in greater or less quantity in the amalgam limb of the zinc cell seems to be unavoidable. Even when using materials of the highest purity, yielding cells of high constancy and reproducibility, some gas is eventually formed. In a series of tests using materials of the highest purity, the following facts have been established:

A sealed tube, containing only zinc amalgam in contact with saturated zinc sulphate solution and zinc sulphate crystals, showed the formation of gas to be independent of the cathode limb of the cell and of the platinum wire immersed in the amalgam. The gas formed in sealed tubes increased greatly in amount (1) in the presence of a small added quantity of free acid, (2) on embedding a platinum wire in the amalgam, and (3) on the addition of mercurous sulphate, which condition may be regarded as similar to (1), in case the mercurous sulphate contains a small amount of free acid or in case of its hydrolysis. The fact that the mercurous sulphate became yellowish would seem to indicate hydrolysis.

A considerable pressure of gas developed in the sealed tubes used in the above experiments, the expansion in volume on release indicating at least one atmosphere. Similar pressures doubtless develop in zinc standard cells with time. The presence of hydrogen or the pressure it exerts seems to have no appreciable effect on the electromotive force of the cell when the latter is measurable. It seems probable that gas is formed because of a slight acidity of the zinc sulphate solution, or because of the gradual diffusion of acid from the cathode limb, in case the mercurous sulphate used as a depolarizer contains free acid or hydrolyzes into free acid and a basic sulphate in saturated zinc sulphate solution. No gas is noticed when zinc amalgam is sealed up with water alone for a considerable period.

Some zinc cells which failed through the lifting of the crystals covering the amalgam by the gradual formation of gas are shown in Fig. 6. The lifting of the crystals would not occur but for the "caking" or sintering of the crystals, which takes place when the temperature of the cell is raised and afterwards lowered. If the

temperature of the cell could be held constant to within 0.01 degree continuously, or subjected only to a rise in temperature, no trouble of this kind would ensue, since bubbles of gas would escape through the loose mass of crystals. The interruption of the electrical continuity of the cell can be remedied by warming the amalgam limb and shaking down the crystals, a procedure not always a successful one, and one which is considered to be rather rough treatment for permanent standards.

The deleterious effect of gas formation has been minimized by using but a small excess of zinc sulphate crystals, a thin layer easily broken up. Such a procedure has proved very successful in the series of 18 cells, the negative terminals of which were pretreated with the zinc amalgam. In setting up the 20 cells with the side limbs sealed at the top with Khotinski cement no particular attention was given to the quantity of crystals added, and considerable trouble developed on account of gas formation as shown in Fig. 6.

In case the crystals in the two limbs of the cell are at different levels, there is a distinct tendency for them to reach the same level. In all of the cells of the group of 18 there has been a gradual deepening of the layer of crystals on the amalgam, thus tending to increase the difficulty of releasing any gas that might be formed. In most of these cells the crystals on the surface of the paste have disappeared entirely and are doubtless leaching from the paste which originally contained about 50 per cent zinc sulphate crystals. The transfer of crystals is probably the result of changes in temperature of the cells, it having been necessary to regulate the standard cell baths at a higher temperature in summer than in winter, the difference in the two regulating temperatures being about 3° and the change being made in a relatively short time. On increasing the temperature the solution in the cathode limb becomes saturated more rapidly than does the greater volume of solution in the amalgam limb, with a consequent diffusion of a portion of the zinc sulphate from the former to the latter. On cooling, the solution in both limbs being saturated, there is no diffusion, and the greater amount of new crystals is thrown down from the greater volume of solution—that is, in the amalgam limb.

The remedy for this is obvious. Where thin layers of crystals are to be used, the surfaces of the amalgam and the paste should be at the same level. This can be done either by shortening the amalgam limb of the cell, by increasing the depth of the layer of

amalgam, or by decreasing the total depth of the paste and mercury. The transfer of crystals has not been noticed in the cadmium cell, doubtless because of the lesser solubility of the cadmium sulphate crystals with temperature.

IV. SUMMARY

1. The ordinary hermetically sealed zinc (Clark) standard cell is subject to two types of failure—cracking at the amalgam terminal and the interruption of the circuit by the gradual formation of gas in the amalgam limb—which greatly reduce its usefulness as a permanent standard of electromotive force.

2. The first type of failure may best be remedied by employing as the amalgam terminal platinum wire previously subjected for a short time to the action of hot 10 per cent zinc amalgam, using a lead sealing-in glass. It seems likely that it can also be remedied by the employment of blanks made entirely of Jena 397^{III} glass, or by using this glass as a sealing-in glass.

3. The second type of failure may be reduced to a minimum by using the smallest excess of crystals required to insure saturation at the highest temperature at which the cell is likely to be used. It is important that the layer of crystals over the amalgam be of small depth and that the surface of the paste and the surface of the amalgam be at approximately the same level.

WASHINGTON, February 27, 1920.